

I have ascertained that toluidine furnishes, both with kinone and chloranile, analogous compounds. The higher percentage of carbon observed by M. Hesse may possibly find a satisfactory explanation in the contamination with toluidine of the aniline which has served for his experiments. Commercial aniline invariably contains more or less toluidine.

V. "Researches on Colouring Matters derived from Coal-tar.—  
I. On Aniline-yellow." By A. W. HOFMANN, LL.D., F.R.S.  
Received June 29, 1863.

In a short paper submitted to the Royal Society in the commencement of last year, I have described a few experiments on the remarkable new colouring matters derived from aniline, which of late have attracted such general attention. This paper had more particularly reference to aniline-crimson, the industrial production of which, in the hands of Mr. E. Nicholson, has reached so high a degree of perfection that the analysis of this compound and of its numerous salts presented no serious difficulty. But the problem was not solved by establishing the formula of rosaniline and its salts: by far the more important obstacles remained to be conquered; the molecular constitution of rosaniline, on which at that time I had not even been able to offer an hypothesis, and the genesis of this well-defined triamine from aniline, had still to be traced. Since that time considerable progress has been made towards the solution of this problem. Some of the latest observations which I have had the honour of submitting to the Royal Society will doubtless help to untie this knot. Nevertheless many doubtful points still remain to be cleared up, and I found it desirable for the better elucidation of the subject to investigate simultaneously several of the other artificial organic colouring matters, in order to trace if possible analogies of composition and constitution in these substances, which, it was reasonable to hope, would throw some light upon the principal subject of the inquiry.

The present moment appeared to be particularly appropriate for an investigation of this kind. The International Exhibition has brought together a collection of these new bodies, such as no other occasion could possibly have assembled in one place and at one time, displaying in a remarkable manner the rapidity with which the industry of our time assimilates and, in many cases, anticipates the results of pure science.

I have commenced the study of a few of the new colouring matters which several of the distinguished exhibitors of these compounds have placed at my disposal—a study which has been greatly facilitated by the zeal and experimental skill of a young chemist, Dr. A. Geyger, who has assisted me in these experiments. Owing to the number of these substances, and in some cases the difficulties of the reactions to be disentangled, some time must elapse before their investigation can be finished,

and I therefore beg leave to submit to the Royal Society the results of these researches as they present themselves. These Notes must necessarily be of a somewhat fragmentary character; but I hope to collect the results thus gradually accumulating, and to lay them before the Royal Society in more logical order and a more elaborated form. I begin the account of this series of experiments with the description of a yellow colouring matter which is obtained as a secondary product in the manufacture of rosaniline.

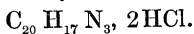
*Chrysaniline*.—It is well known that even in the most successful operation, and whatever the process of preparation may be, the rosaniline produced is only a small percentage of the aniline employed. Together with the crimson-colour a large proportion of a resinous substance of feebly basic properties is formed, the generally ill-defined characters of which have hitherto baffled all attempts at a thorough investigation. This mixture contains nevertheless several individual compounds, which may be extracted with boiling water, and subsequently separated by treatment with reagents. Mr. E. C. Nicholson has thus isolated a magnificent yellow colouring matter. Considerable quantities of this interesting body, Mr. Nicholson with his usual liberality has placed at my disposal, for which my best thanks are due to him.

The yellow colouring matter, for which, on account of the splendid golden-yellow tint it imparts to wool and silk, and in order to record its origin, I propose the name of *chrysaniline*, presents itself in the form of a finely divided yellow powder, closely resembling freshly precipitated chromate of lead, perfectly uncrystalline, scarcely soluble in water, which it just colours, easily soluble in alcohol and in ether. This compound is a well-defined organic base, which forms with the acids two series of crystallized saline compounds. The most characteristic salts of chrysaniline are the nitrates, more especially the mononitrate, which is difficultly soluble in water, and crystallizes with facility. It was from this compound, purified by half a dozen crystallizations, that I prepared the chrysaniline for analysis. An aqueous solution of the pure nitrate decomposed with ammonia yields the chrysaniline in a state of perfect purity. The analysis of this substance, dried at 100°, has furnished results which may be translated into the formula

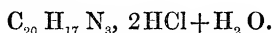


This expression is corroborated by the examination of several salts, more especially the beautiful compound which this base produces with hydrochloric acid.

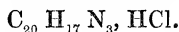
*Hydrochlorate of Chrysaniline*.—On adding concentrated hydrochloric acid to a solution of chrysaniline in the dilute acid, a scarlet crystalline precipitate is produced, consisting of minute scales very soluble in water, less soluble in alcohol, almost insoluble in ether. These crystals constitute the diacid chloride of chrysaniline,



Under conditions not yet sufficiently defined, this substance is precipitated with water of crystallization as

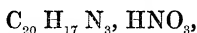


For analysis these salts were dried at  $100^\circ$  or  $120^\circ$ , at which temperature they remain quite unchanged. When heated more strongly they lose hydrochloric acid. When the diacid chloride is maintained for a fortnight between  $160^\circ$  and  $180^\circ$ , the weight of the salt again becomes constant. The residuary yellow crystalline powder, differing from the original hydrochlorate only by its somewhat diminished solubility in water, was by analysis found to be the pure monacid hydrochlorate of chrysaniline,

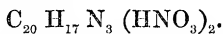


The crystalline compounds which chrysaniline forms with hydrobromic acid and hydriodic acid are perfectly analogous to the salts produced by hydrochloric acid. I have not analyzed them.

The *nitrates of chrysaniline* are the finest salts of this base; these compounds crystallize with the utmost facility in ruby-red needles, which are remarkably insoluble in water. A dilute solution of nitric acid (1 grm. of  $\text{HNO}_3$  in a litre of water), when mixed with moderately dilute solutions of the chloride, yields immediately a crystalline precipitate, so that soluble chrysaniline salts might be used as a test for nitric acid. For the same reason nitric acid is conveniently employed in separating chrysaniline from the crude liquid obtained by boiling out the secondary products of the manufacture of rosaniline. Nevertheless the preparation of the nitrates presents unusual difficulties, and I have lost much time in endeavouring to fix the conditions under which the monacid and the diacid salts may be separately produced. On boiling an excess of free chrysaniline with dilute nitric acid, a solution is obtained depositing, on cooling, needles which are the mononitrate,



in a state approaching purity. On pouring the solution of this salt into cold concentrated nitric acid, a salt is at once precipitated which crystallizes in ruby-red prisms very similar to ferricyanide of potassium, and constitutes the nearly pure dinitrate,



But here also analysis exhibits slight discrepancies, indicating the presence of traces of the former compound. By treatment with water the dinitrate gradually loses its nitric acid, and after two or three crystallizations it is converted into the mononitrate.

The *sulphate* is very soluble, scarcely crystalline.

The platinum-salt is a splendid scarlet crystalline precipitate, which, from hot and rather dilute solutions containing much free hydrochloric acid, is often deposited in very fine and large plates. All my attempts to obtain this substance in a state of purity have failed. The platinum percentages vary with every new preparation, indicating the formation of a

monochloroplatinate and a dichloroplatinate, combining with more or less water of crystallization.

The composition of chrysaniline places this substance in immediate juxtaposition with rosaniline and leucaniline. These three triamines simply differ by the amount of hydrogen which they contain.

|                    |                   |
|--------------------|-------------------|
| Chrysaniline. .... | $C_{20}H_{17}N_3$ |
| Rosaniline .....   | $C_{20}H_{19}N_3$ |
| Leucaniline .....  | $C_{20}H_{21}N_3$ |

Chrysaniline is monacid or diacid; rosaniline monacid or triacid, but with essentially monacid predilections; leucaniline forms exclusively triatomic compounds.

The formula of chrysaniline suggests the possibility of transforming this substance into rosaniline and leucaniline, or of producing chrysaniline from rosaniline or leucaniline. Up to the present moment this transformation has not been experimentally accomplished. The constitution and genesis of chrysaniline remain to be made out.

VI. "Researches on the Colouring Matters derived from Coal-tar.—  
II. On *Aniline-blue*." By A. W. HOFMANN, LL.D., F.R.S.  
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Among the several stages which mark the development of the industry of coal-tar colours, the discovery of the transformation of aniline-red into aniline-blue will always hold a prominent position. This transition, for the first time observed by MM. Girard and De Laire\*, two young French chemists of M. Pelouze's Laboratory, and subsequently matured by M. Persoz, De Laynes, and Salvétat†, has become the foundation of an enormous industrial production, which, having received a powerful impulse by MM. Renard Brothers and Franc in France, and more recently by Messrs. Simpson, Maule, and Nicholson in this country, has rapidly attained to proportions of colossal magnitude.

The transformation of aniline-red into aniline-blue is accomplished by a process of great simplicity, and consists, briefly expressed, in the treatment at a high temperature of rosaniline with an excess of aniline. The mode of this treatment is by no means indifferent. Rosaniline itself cannot in this manner conveniently be converted into the blue colouring matter; the transformation is, however, easily accomplished by heating rosaniline salts with aniline, or, *vice versâ*, rosaniline with salts of aniline. Again, the nature of the acids with which the bases are combined is by no means without influence upon the result of the operation; manufacturers give a decided preference to organic acids, such as acetic or benzoic acids.

The production of the new colouring matter on a very large scale has already elicited a good deal of most valuable information regarding the

\* French patent, January 1861.

† Comptes Rendus, March and April 8th, 1861.